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Review

# Processable Low-Bandgap Polymers for Photovoltaic Applications†

Pierre-Luc T. Boudreault, Ahmed Najari, and Mario Leclerc*

*Canada Research Chair on Electroactive and Photoactive Polymers, Department of Chemistry, Université Laval, Quebec City, Quebec, Canada G1V 0A6*

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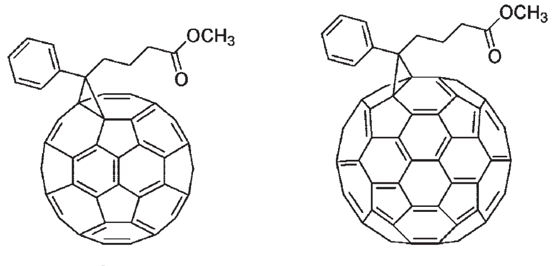
Over the last five years, organic photovoltaic devices have emerged as a new competitor to silicon-based solar cells. In particular, the bulk heterojunction architecture (BHJ), in which the photoactive layer consists of a bicontinuous blend of an electron donor and an electron acceptor, has allowed power conversion efficiencies around 8%. We will present in this review the latest conjugated polymers used in such BHJ solar cells. We will mainly focus on electron-donating (*p*-type) polymers based on thiophenes, 1,3,2-benzodiathiazoles, pyrrolo[3,4-*c*]pyrrole-1,4-diones, benzo[1,2-*b*;3,4-*b*]-dithiophenes, and few other materials with more exotic structures. This review should be helpful to evaluate which are the most promising materials and where this research field is going in the years to come.

## 1. Introduction

The utilization of the photovoltaic effect to generate electricity from solar energy represents an appealing solution to our growing need for clean, abundant, and renewable energy sources, and to our desire for protecting the environment. Unfortunately, up to now, only a very small percentage of the energy production comes from the sun,[1] mainly because of the relatively high cost of the silicon-based solar cells.[2] Organic photovoltaic cells (OPVs) are viewed as one of the most promising candidates for low cost solar cells because of the possibility of a production on flexible and large-area substrates by solution processing that should dramatically reduce the manufacturing costs.[3−5]

Along these lines, solar cells based on blends of conjugated polymers and [6,6]-phenyl $C_{61}$-butyric acid methyl ester ($PC_{61}BM$) have been investigated extensively in the past decade.[6] For this purpose, many new low bandgap polymers have been developed.[7] We will present in this Review most of these new polymers and will describe their strengths and weaknesses for the fabrication of OPVs. We will mainly focus on the performances of the polymers utilized as electron donors in the bulk heterojunction (BHJ) architecture.[4,5,8,9] The BHJ concept has been widely applied for the fabrication of polymer-based solar cells because it generates a bicontinuous network between an electron donor and an electron acceptor and also maximizes the light absorption in the active layer.[9] We will not discuss the electron acceptors because most of the performances that will be presented were obtained with $PC_{61}BM$ or $PC_{71}BM$;[10] their chemical structure being presented in Figure 1.[11,12] Much efforts have been devoted to the synthesis of new electron acceptors and despite some interesting results leading to a better understanding of the active layer;[13] the performances are still much lower when compared with fullerene derivatives.



$PC_{61}BM$ $PC_{71}BM$

**Figure 1.** Chemical structures of the most used electron acceptors for BHJ solar cells ($PC_{61}BM$ and $PC_{71}BM$).

From an industrial point of view, solar cells should exhibit a power conversion energy (PCE) of around 10%.[14] Few years ago, this milestone seemed very difficult to reach but recent developments have allowed a PCE above 8%.[15] Therefore, this goal does seem more and more realistic. To reach such PCEs, chemists have to come up with new structures that should allow a fine-tuning of the properties. In concrete terms, when blended with PCBM, the requirements are a HOMO energy level lower than −5.20 eV to increase the $V_{OC}$ of the device and to get an air-stable material together with a bandgap ($E_g$) between 1.30 and 1.90 eV to absorb efficiently the sunlight. The hole mobility of the pristine polymer should also be greater than $1 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$.[14] As we wrote in 1989, only those conjugated polymers that are able to combine good transport, optical, and mechanical properties together with processability and environmental stability have chances to be utilized toward the production of electronic or optical devices. Among the many factors which influence the overall performances of a polymer with regard to the transport properties in combination with useful mechanical properties, the structural regularity and the molecular

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*Corresponding author. E-mail: mario.leclerc@chm.ulaval.ca.

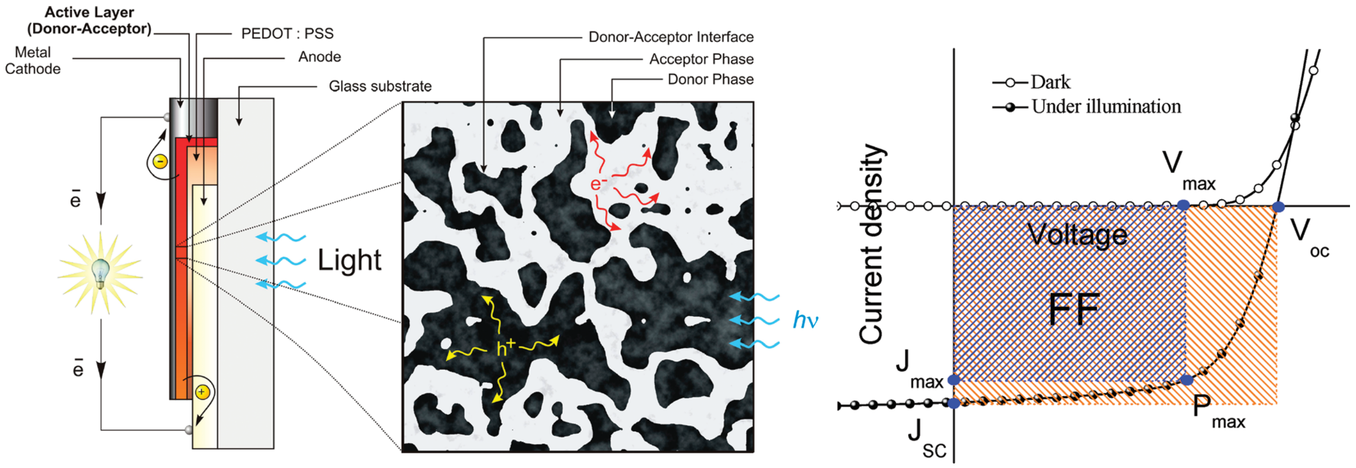

**Figure 2.** Schematic illustration of donor−acceptor BHJ solar cell, with a magnified area showing the morphology of the active layer. PEDOT:PSS is poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate. The typical current−voltage characteristics for dark and light current in photovoltaic cell device illustrate the essential parameters: $J_{max}$ and $V_{max}$ are the current and voltage at the maximum power point ($P_{max}$), $J_{sc}$ is the short-circuit current density, $V_{oc}$ is the open circuit voltage and FF is the fill factor. The power conversion efficiency (PCE) is defined as the ratio of power out ($P_{out}$) to power in ($P_{in}$) and closely related to FF, $J_{sc}$, and $V_{oc}$.

weight are the most decisive.[16] Interestingly, in the following sections, we will mainly refer to the number-average molecular weights ($M_n$) instead of the weight-average molecular weights ($M_w$). The $M_n$ does have a direct relationship to the degree of polymerization, which has a strong impact on the physical properties of the resulting polymers.

The morphology of the blend is another important parameter to achieve high PCEs. Indeed, the electron acceptor and the electron donor should form a bicontinuous network (i.e., BHJ architecture) with domain widths twice that of the exciton diffusion length, as illustrated in Figure 2.[17] This blend should then allow a high interfacial area to optimize the exciton dissociation and efficient transport of the generated charges to their respective electrodes. Obviously, it is very difficult to obtain all of these characteristics at once within any polymer and fullerene derivative pair. Several processing parameters can be therefore modified to optimize the performances of a particular blend. For example, the solvent used, the concentration of the solution deposited as the active layer, the donor/acceptor ratio, the spinning rate during the deposition, the drying temperature of the films (annealing) can also affect the overall performances. To have the best possible device, all these parameters have to be optimized. Other parameters that have not been thoroughly investigated over the years are the thickness of the active layer and the size of the active area. These two parameters do not require much attention for laboratory-scale experiments; however, for industrial applications, researchers will have to solve some issues related to large-scale and low-cost production. For example, most of the performance reported in this Review implies an active layer thickness around 80−100 nm. In contrast, for an industrial roll-to-roll processing, a minimum thickness of 150−200 nm may be required. Also, since the commercial devices will possess an active area of at least 1 cm$^2$, larger devices have to be fabricated and tested to reflect the needs of the industry.

The first few polymers that were developed for organic photovoltaic cells (OPVs) are the regioregular poly(3-hexylthiophene) (rr-P3HT)[18,19] and poly(1,4-phenylene-vinylene)s (PPVs),[20] especially poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene-vinylene] (MDMO-PPV), which was extensively studied.[11,21] However, their bandgaps and electronic properties are not optimal for solar cell applications and it is difficult to synthesize derivatives of these two classes of polymers where the bandgap will be much lower and not lose at the same time their good morphology and hole mobility.[22] After several years of optimization, PCEs of around 5−6% have been achieved with P3HT and around 2−3% with different PPV derivatives. Even though these improvements are quite noticeable, there is clearly a need for better materials and related devices. As mentioned above, it is therefore the aim of this review to present new electron-donating low-bandgap polymers used in BHJ solar cells; namely polythiophenes, polybenzodiathiazoles (BT), poly(pyrrolo[3,4-*c*]pyrrole-1,4-dione)s, which is also named poly(diketopyrrolopyrrole)s (DPP), poly(benzo[1,2-*b*:4,5-*b*′]dithiophene)s (BDT), and some other more exotic conjugated polymers.

## 2. Polythiophene Derivatives

Figure 3 shows the different polythiophene derivatives that have been synthesized for solar cell applications. Over the years, several groups reported that the presence of alkyl side chains is a convenient method to get processable polythiophene derivatives.[23] In particular, the popularity of P3HT (**P1**) exploded when McCullough et al. reported an efficient method for polymerizing 3-alkylthiophenes in a head-to-tail fashion without any major defect.[24] Their method is straightforward; they generate regiospeficically the 2-bromo-5-bromomagnesio-3-alkylthiophene and the polymerization process is activated in situ by a Kumada cross-coupling reaction. Two other methods were then developed to address the economical issue of this synthesis. First, the Rieke method involves the highly reactive “Rieke zinc” (Zn*) to treat the 2,5-dibromo-3-alkylthiophene[25] where an organozinc intermediate is used with a palladium catalyst (Pd(PPh$_3$)$_4$) to yield regioregular poly(3-alkylthiophene)s (P3ATs). The second

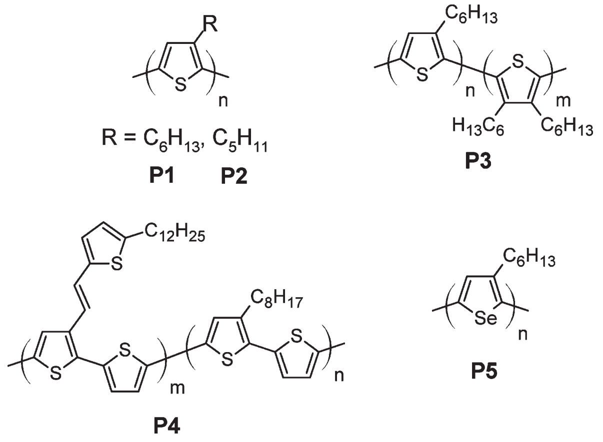

**Figure 3.** Polythiophene derivatives for photovoltaic cell applications.

one is called the "GRIM method", where there is no need to utilize either very low temperatures or highly reactive metals. This is the easiest method to produce different high-molecular-weight rr-P3ATs on a kilogram scale. In this method, 2,5-dibromo-3-alkylthiophene is treated with 1 equiv. of a Grignard reagent where two regioisomers are obtained in a 80:20 ratio, the major regioisomer being the desirable product. The polymerization reactions occurs in the presence of a nickel catalyst, usually Ni(dppp)$Cl_2$. Even with the ratio mentioned before, after the polymerization is completed, more than 99% of the polymer obtained is regioregular. Since then, rr-P3HT has become the most-studied conjugated polymer in organic field-effect transistors (OFETs) because of its ability to well-organize in three dimensions, leading to good interchain and intrachain charge carrier pathways.[26] Later on, also rr-P3HT became the most popular polymer for photovoltaic applications.

The P3HT/PCBM blend probably reached its full potential when Heeger et al. were able to obtain a PCE of 5.1% with this particular material.[19] Since then, numerous groups are still trying to increase the performances by modifying the morphology, the device architecture, and the electron acceptor, but this research has not led to any significant improvements in the PCE.[5] Many studies on the influence of the molecular weight on the performances have also been reported.[27] The main issue with P3HT is its quite large bandgap (1.9−2.0 eV), which limits the light absorption from the solar spectrum. Interestingly, Plextronics was recently able to reach performances around 6% with rr-P3HT but with a new fullerene derivative.[28]

Because the organization of a material is strongly dependent on the nature of the side chains, Jenekhe et al. studied the effect of the chain length.[29] Pentyl side chains (**P2**) seemed an interesting candidate to investigate the effect of having whether an odd or even number of carbon atoms in the alkyl chain. Even with these shorter side chains, they were still able to get a number-average molecular weight ($M_n$) of around 77 kDa. They were able to obtain a power conversion efficiency of 3.7% with an optical bandgap of 1.9 eV. It does seem that this material could be more useful as the active layer in OFETs because of the formation of nanowires during the processing of the films. In parallel, instead of modifying the chain length on the backbone, Fréchet et al. focused on the synthesis of block copolymers bearing a small amount of 3,4-dihexylthiophene (**P3**).[30] This strategy did not allow better photovoltaic performances. However, it was found that the addition of a small amount of another monomer does allow a much better stability of the devices.

Polythiophene derivatives are usually made of aliphatic side chains but Li et al. synthesized a two-dimensional conjugated network by adding a conjugated side chain at the 3-position of the thiophene.[31] The goal of adding a bis(thienylenevinylene) side chain on the thiophene was to force a broader absorption of the polymer and consequently, to obtain a better match of the solar spectrum. However, the performances were still lower than what has been presented earlier for rr-P3HT. The best PCE was 3.2%.

A completely different strategy to lower the bandgap of rr-P3HT was the synthesis of regioregular poly(3-hexylselenophene) (rr-P3HS). Ballantyne et al. successfully completed the synthesis of this polymer for OPVs.[32,33] They obtained a $M_n$ of 70 kDa. The optical bandgap (i.e., 1.60 eV) of the resulting polymer was also much lower that the rr-P3HT counterpart. The cells were fabricated following similar conditions but the PCE was lower with best performances near 2.7%. The authors mentioned that future studies will focus on the modifications of the morphology of the films. Just like P3HT, P3HS has a strong tendency to crystallize, especially upon annealing.

Up to now, almost every side chain length has been tested (from butyl to octadecyl) but the performances are still better with P3HT.[34] The performances of polythiophene derivatives are relatively stable since 2005, with PCEs up to 5−6% (see Table 1) and that explains why new conjugated polymers have been recently developed.

## 3. Push−Pull Copolymers

**3.1. 2,1,3-Benzodiathiazole Derivatives.** One of the most efficient ways to lower the bandgap of a polymer is by combining two comonomers, one being an electron-rich (fluorene, carbazole, dibenzosilole, benzodithiophene, etc.) and the other one being an electron-deficient moiety (benzodiathiazole, diketopyrrolopyrrole, etc.). As shown in Figure 4, a wide variety of such push−pull copolymers have been recently synthesized with bandgaps ranging from 1.0 to 2.0 eV. The main challenge for solar cell applications is to find the right copolymers that will allow an efficient morphology of the films while keeping good charge carrier properties at the same time. One of the most studied electron-deficient units is certainly the benzodiathiazole moiety. There are two types of comonomers that were developed for solar cell applications. The easiest way is the use of 2,1,3-benzodiathiazole (BT) directly with the other comonomer. The other possible comonomer is the 4,7-dithien-5-yl-2,1,3-benzodiathiazole (DTBT) where there are two thiophene spacers between the BT unit and the electron-rich unit. The performances of all these copolymers are summarized in Table 2. The synthesis of these polymers is usually performed either by Suzuki or Stille cross-coupling reaction. The addition of these two

**Table 1. Summary of the OPV Performances of the Polythiophene Derivatives**[a]

| polymer | $M_n$ (PDI) (kDa) | $E_g^{opt}$ (eV) | HOMO/LUMO (eV/eV) | donor:PCBM ratio (wt:wt) | $J_{sc}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | PCE (%) | active area (mm$^2$) | ref |
|---|---|---|---|---|---|---|---|---|---|---|
| **P1** | N.A | N.A. | N.A. | 1:0.8 | 9.50 | 0.63 | 0.68 | 5.1 | 15 | 19 |
| **P2** | 77 (1.4) | 1.90 | N.A. | 1:1[b] | 9.63 | 0.56 | 0.69 | 3.7 | 3.6 | 29 |
| **P3** | 22 (1.3) | N.A. | N.A. | 1:1 | 10.3 | 0.61 | 0.60 | 3.7 | N.A. | 30 |
| **P4** | 50 (1.6) | 1.82 | −4.93/−2.96 | 1:1 | 10.3 | 0.72 | 0.43 | 3.2 | 4 | 31 |
| **P5** | 70 (2.9) | 1.60 | −4.80/−3.20 | 1:1 | ~6.5 | 0.52 | N.A. | 2.7 | N.A. | 32 |

[a] $M_n$ is the number-average molecular weight. PDI is the polydispersity index ($M_w/M_n$). $E_g^{opt}$ is the optical bandgap, measured in the solid state. The HOMO level is the highest occupied molecular orbital and the LUMO level is the lowest unoccupied molecular orbital, both are measured by electrochemistry method in the solid state. $J_{SC}$ is the short-circuit current density, the $V_{OC}$ is the open circuit voltage, and FF is the fill factor. [b] The electron acceptor used is $PC_{71}BM$.

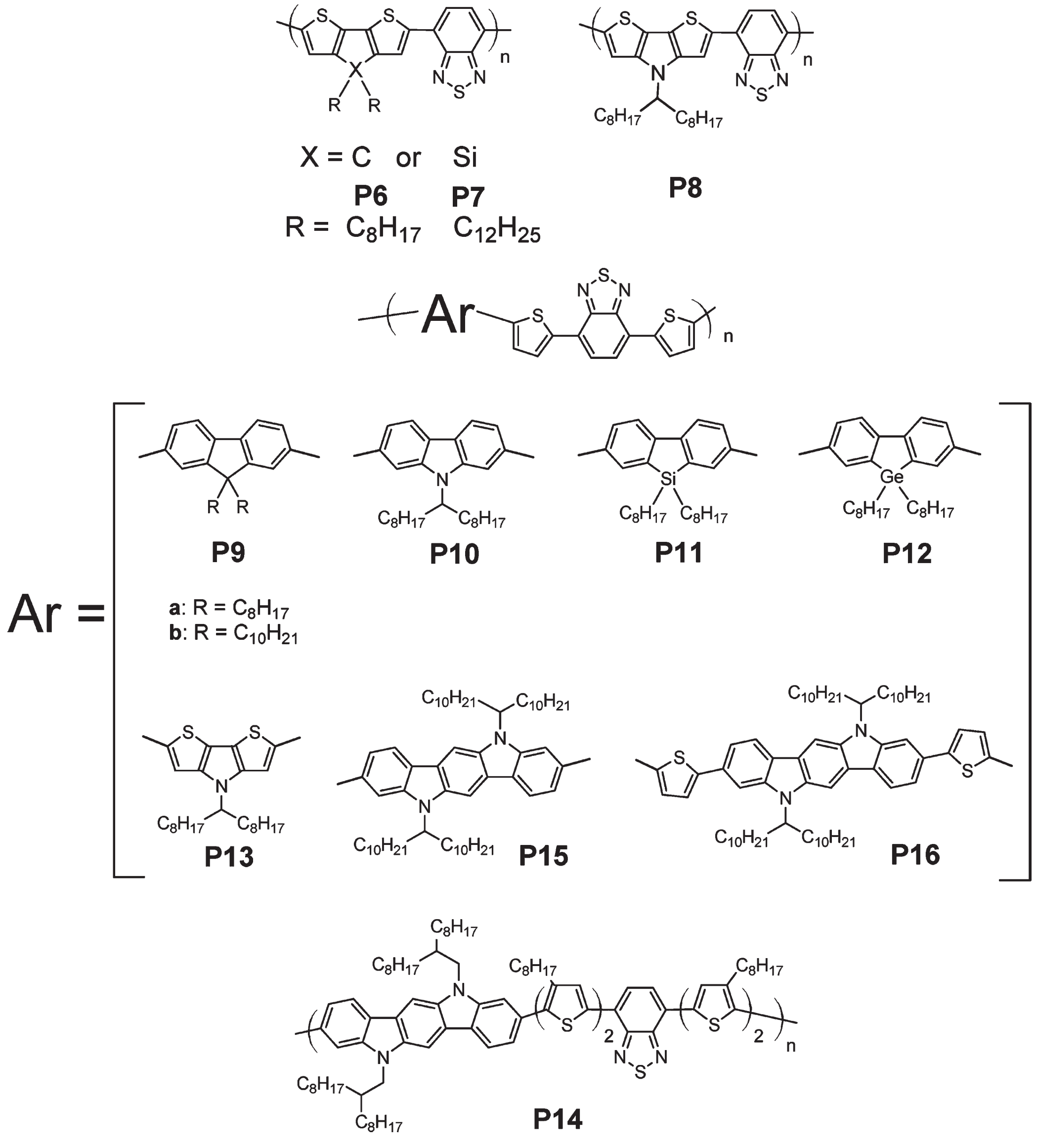

**Figure 4.** Push−pull copolymers with benzodiathiazole as the electron-deficient unit.

thiophene units allows the synthesis of coplanar copolymers. This is especially important when using comonomers such as fluorenes, carbazoles, or dibenzosiloles, because these monomers are based on a biphenyl unit. If these molecules were polymerized directly next to the BT unit, it would create important steric hindrance between the monomers resulting in an important torsion angle. Twisted polymers are not desirable for OPVs because of their larger bandgaps and poor interchain interactions. For these reasons, the BT unit is mainly employed for the synthesis of copolymers with comonomers based on dithiophene units.

There are two dithiophene-based units that have been more extensively studied over the years, namely cyclopentadithiophene and dithienosilole. Poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b′]-dithiophene)-*alt*-4,7-(2,1,3-benzodiathiazole)] (**P6**) has first attracted much

**Table 2. Summary of the OPV Performances of the Push−Pull Copolymers Based on the Benzodiathiazole Moiety**

| polymer | Mn (PDI) (kDa) | $E_g$ (opt) (eV) | HOMO/LUMO (eV/eV) | donor:PCBM ratio (wt:wt) | $J_{sc}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | PCE (%) | active area (mm$^2$) | ref |
|---|---|---|---|---|---|---|---|---|---|---|
| **P6** | 35 (1.3) | 1.40 | −5.30/−3.57 | 1:2−3[a] | 16.2 | 0.62 | 0.55 | 5.5 | 17 | 38 |
| **P7** | 44 (2.0) | 1.37 | N.A. | 1:1[a] | 17.3 | 0.57 | 0.61 | 5.9 | 17 | 37 |
| **P8** | 18 (1.6) | 1.43 | −4.81/−3.08 | 1:3 | 11.9 | 0.54 | 0.44 | 2.8 | 12 | 45 |
| **P9-a** | 4.8 (2.9) | N.A. | N.A. | 1:4 | 4.66 | 1.04 | 0.46 | 2.2 | 100 | 46 |
| **P9-b** | 9.7 (3.6) | N.A. | N.A. | 1:4 | 7.70 | 1.00 | 0.54 | 4.2 | 36 | 47 |
| **P10-a** | 37 (2.0) | 1.88 | −5.50/−3.60 | 1:4 | 6.92 | 0.89 | 0.53 | 3.6 | 90 | 48 |
| **P10-b** | 19 (2.1) | 1.88 | −5.50/−3.60 | 1:4[a] | 10.6 | 0.88 | 0.66 | 6.1 | 13 | 49 |
| **P11-a** | 15 (1.3) | 1.86 | −5.70/−3.81 | 1:4 | 2.80 | 0.97 | 0.55 | 1.6 | 25 | 50 |
| **P11-b** | 79 (4.2) | 1.82 | −5.39/N.A. | 1:2 | 9.40 | 0.90 | 0.51 | 5.4 | 15 | 51 |
| **P12** | 10 (2.4) | 1.79 | −5.58/−3.91 | 1:2 | 6.90 | 0.79 | 0.51 | 2.8 | 100 | 52 |
| **P13** | 1.8 (3.4) | 1.46 | −5.00/−3.43 | 1:1 | 9.47 | 0.52 | 0.44 | 2.2 | 6 | 53 |
| **P14** | 20 (2.1) | 1.89 | −5.17/−3.15 | 1:2 | 9.17 | 0.69 | 0.57 | 3.6 | 35 | 54 |
| **P15** | 18 (1.9) | 1.91 | −5.45/−3.55 | 1:3 | 3.77 | 0.94 | 0.41 | 1.5 | N.A. | 55 |
| **P16** | 8.6 (1.6) | 1.85 | −5.43/−3.62 | 1:3 | 4.83 | 0.90 | 0.48 | 2.1 | N.A. | 56 |

[a] The electron acceptor used is PC$_{71}$BM.

attention with a PCE of 3.2%.[35] This polymer has two important assets. First, its bandgap is quite low (1.4 eV); second, as demonstrated by Müllen et al., **P6** can exhibit a hole mobility as high as 1.4 cm$^2$ V$^{-1}$ s$^{-1}$ in optimized conditions.[36] Bazan et al. also showed that it is possible to optimize the molecular weight of this polymer through a synthesis under microwave conditions.[37]

Heeger et al. optimized as much as possible the performances of this material by using PC$_{71}$BM and by introducing a certain amount of additives (i.e., 1,8-octanedithiol) for the preparation of the films.[38] At this point, the performance reached 5.5%, even though the open circuit voltage ($V_{OC}$) of the devices is rather low at 0.62 V. The value is very well compensated with a very good short circuit current density ($J_{SC}$) of 16.2 mA/cm$^2$ and a fill factor (FF) of 55%. Other additives were utilized during the processing of the films but the efficiencies were lower.[39] Moreover, there are some concerns about the stability of this polymer. One of these concerns is toward the carbon atom on top of the five-membered ring that could undergo an oxidation into a ketone, just as reported for polyfluorenes.[40,41] For this reason, a new derivative, i.e., dithienosilole, was synthesized in order to minimize this type of oxidation. Yang et al. were the first ones to use this comonomer for OPV applications. They showed that by adding ethylhexyl side chains on the silicon atom, the resulting copolymers had a good solubility and high molecular weights. **P7** was prepared from a standard Stille coupling reaction and a $M_n$ of 18 kDa with a polydispersity index (PDI) of 1.2 were obtained. The optical bandgap (1.45 eV) is very close to that of **P6**. It was found that the hole mobility of this polymer is 3 × 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ which is approximately three times higher than the mobility of **P6**. The $V_{OC}$ of **P7** was slightly higher at 0.68 V but the $J_{SC}$ was significantly lower at 12.7 mA/cm$^2$ and that leads to a PCE of 5.1%.[42] Yang et al. showed that the C−Si bond is longer and than C−C bond in the fluorene core. Consequently, there is less steric hindrance created in the dibenzosilole core, leading to a better $\pi$−$\pi$ stacking.[43] This translates in a better hole mobility in OFET devices but did not lead to an improvement of the performances in OPVs. Bazan et al. reported even more impressive results with this particular polymer. They replaced the 2-ethylhexyl chains on the silicon atom by long *n*-dodecyl side chains. They also polymerized by Stille coupling but they used a microwave-assisted method, which led to higher number-average molecular weight of 44 kDa. The PCE of the devices made with this polymer were also higher, reaching a maximum of 5.9%.[37] Polymer **P8** was also synthesized through Stille coupling reaction using the same architecture as mentioned before with the dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) core. The 1-pentylhexyl side chain on the nitrogen atom gave the best results. A reasonable $M_n$ of 18 kDa was obtained and the optical bandgap was very similar to that obtained with cyclopentadithiophene or dithienosilole unit. However, the HOMO and LUMO energy levels are much higher. This could cause some stability issues under ambient conditions. The best solar cell that was fabricated with this material and PC$_{61}$BM (1:3) led to a PCE of 2.8%. The $V_{OC}$ and fill factor were quite low.

Other copolymers with a structure relatively similar to the three previous copolymers have been synthesized. Noticeably, Bazan et al. reported an interesting study based on (poly[(4,4-didodecyldithieno[3,2-b:2′,3′-d]silole)-2,6-diyl-alt-(2,1,3-benzoxazole)-4,7-diyl]).[44] This report showed the importance of an efficient interpenetrating network where the addition of an additive, namely, 1-chloronaphthalene (CN), can help to increase the PCE to much higher levels. During the processing of the films, the addition of only 2% of CN improved the PCE from 1.6% to 5.4%.

The other polymers based on this push−pull system were copolymerized with DTBT and electron-rich biphenyl units such as fluorenes. Poly(2,7-fluorene) derivatives have attracted much attention over the years because of their impressive performances in organic light-emitting diodes (OLEDs).[1] The first polymer that was studied extensively for solar cell applications is polymer **P9**. The polymerization was performed with 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-9-(2″-ethylhexyl)-9-hexylfluorene and DTBT through a Suzuki coupling reaction. The resulting polymer was first published by Andersson et al. in 2003 (**P9-a**).[46] Even though they performed the polymerization with an asymmetrical fluorene-based monomer which should increase the

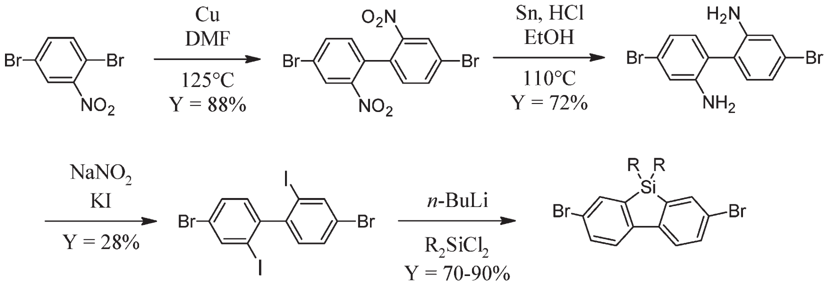

**Figure 5.** Synthetic route of 2,7-dibromodibenzosiloles.

solubility of the polymer, they could only afford rather low molecular weights ($M_n$ of 4.8 kDa). Still, they were able to obtain a power conversion efficiency of 2.2%, which was one of the best values published back in 2003. The $V_{OC}$ values of the devices are very impressive at around 1.0 V, one of the best ever reported for a regular BHJ solar cell. It has to be mentioned that they obtained this PCE with a rather large active area of 100 mm$^2$. Sloof et al., with a fluorene derivative with two decyl side chains instead (**P9-b**) and a $M_n$ close to 10 kDa, were able to reach better performances with a PCE of 4.2%.[47] These performances may also be enhanced by the fact that the active area was much smaller (factor of 3). However, they utilized a very thick active layer (190 nm) and this usually leads to lower performances. The utilization of thicker layers may be important for the development of commercial devices.

On the basis of this study, Leclerc et al. synthesized a wide variety of new low bandgap copolymers based on the carbazole unit. Prior to these promising results, carbazole derivatives were mostly utilized in OLEDs or in OFETs.[57] This study changed the trend. In particular, polymer **P10** has attracted much attention with a PCE of 3.6%.[48,58] The heptadecanyl side chain added on the carbazole backbone represents an important step toward the synthesis of high molecular weight and processable poly(2,7-carbazole)s. For **P10**, the $M_n$ was as high as 37 kDa with a polydispersity index (PDI) of 2.0. Higher $M_n$ can be obtained by extending the polymerization time but it did not lead to better performances. The optical bandgap of this polymer is 1.88 eV with a low-lying HOMO energy level that should provide a very stable polymer under ambient conditions.[59] It was found that by blending **P10** (with an optimized molecular weight of ~20 kDa) with PC$_{71}$BM in a 1:4 ratio, the PCE reached 4.6%.[60] The same team pushed further the optimizations of **P10**. They evaluated that the best film thickness was around 70 nm and with a **P10**:PC$_{71}$BM ratio of 1:4, they were able to increase the performances even more to 5.7% on an active area of 100 mm$^2$.[61] Following these promising results, Heeger et al. further optimized the performances by adding an optical spacer (TiO$_x$) between the cathode (Al) and the active layer (**P10**:PC$_{71}$BM) in order to increase the optical absorption without having to increase the thickness of the active layer.[49] They obtained a power conversion efficiency of 6.1%. One of the most impressive properties is the internal quantum efficiency (IQE), which is close to 100%, meaning that almost every absorbed photon leads to a pair of charge carrier and that nearly all the photogenerated carriers are collected at their respective electrode.

Because of the problems related to the polyfluorenes, like the oxidation into fluorenone, several research groups investigated various heterofluorene derivatives.[40] One of the most obvious choices is the dibenzosilole unit because the silicium atom is located right under the carbon atom in the periodic table. 3,6-Disubstituted dibenzosiloles can be synthesized very easily from 2,2′-dibromobiphenyl. However, polymers based on these comonomers have never achieved great performances in OFETs and OPVs.[62] Because 2,7-disubstituted dibenzosiloles are not as readily available as fluorenes, they have to be synthesized following the procedure presented in Figure 5. Comonomers based on dibenzosiloles were synthesized with different chain lengths (*n*-octyl and 2-ethylhexyl).

The synthesis of these polymers is performed through Suzuki coupling reaction since the diboronic ester is easy to obtain and to purify. Leclerc et al. were the first ones to report a copolymer with DTBT (**P11-a**).[50] With a molecular weight of 15 kDa and an optical bandgap of 1.86 eV, a PCE of 1.6% was obtained. The very low $J_{SC}$ (2.80 mA/cm$^2$) for this device is compensated by the large $V_{OC}$ (0.97 V). Cao et al. were able to obtain the same polymer (**P11-b**) with a molecular weight as high as 79 kDa.[51] This parameter certainly had a major impact on the performances of the device made from **P11**. The short circuit current density was more than three times higher (reaching 9.80 mA/cm$^2$) than the one previously reported. The higher molecular weight also had an effect on the field-effect mobility of the polymer where they were found to be 1 order of magnitude higher than that of **P11-a**. A PCE of 5.4% is very impressive and clearly confirms that polydibenzosilole derivatives are a very competitive class of electron-donating polymers for solar cell applications. It also means that molecular weights are important parameters in organic electronics. It seems that many polymers tend to have better performances with higher molecular weights but it is not necessarily the case with all polymers. Consequently, it is important that all promising polymers undergo a complete optimization of their molecular weights to obtain the best possible performances.

Another electron-rich comonomer that has been investigated very recently for organic electronics is the 2,7-germafluorene unit. The first report of polymers based on this type of unit was done by Huang et al. where they polymerized 2,7-fluorene with only a small amount of a germafluorene derivative (10%) in a random polymerization.[63] This small amount did not greatly affect the performances and there was still a need to develop homopolymer and alternating copolymer derived from germafluorenes. The 2,7-germafluorene monomer was obtained using the same strategy developed for dibenzosiloles to afford polymer **P12**. However, the final ring closure has to be performed under Schlenk conditions considering the high reactivity of the germane precursor. The polymerization reaction was again performed through Suzuki coupling and a $M_n$ of 10 kDa with a PDI of 2.4 was obtained. The fabrication of solar cells from this polymer led to PCE of 2.8%. The $V_{OC}$ (0.79 V) is smaller than other derivatives based on a similar architecture but the $J_{SC}$ is good at 6.90 mA/cm$^2$.[52]

Dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) is another strong electron-rich unit suitable for the synthesis of push−pull polymers. This unit was first studied in field-effect transistors.[64] A hole mobility around 0.1 cm$^2$ V$^{-1}$ s$^{-1}$ was reported some polymeric materials. Meanwhile, Hashimoto et al. also used the DTP unit for OPVs. Copolymers with DTBT (**P13**) unit exhibited low molecular weight (1.8 kDa) with a PDI of 3.4 but the bandgap for this polymer was very interesting at 1.46 eV. Even with this very low $M_n$, the PCE was still at 2.2%, which is in part due to the impressive $J_{SC}$ (9.47 mA/cm$^2$). However, in order to reach higher performances, the $V_{OC}$ will have to be much higher than 0.52 V.

Finally, the last comonomer that will be described in this section is the indolo[3,2-*b*]carbazole (IC). IC-based materials have been studied extensively over the past years, mainly for FET applications.[57] At first, small molecules were synthesized with a high level of crystallinity.[65] The best hole mobility in OFET devices obtained with this type of materials is 0.22 cm$^2$ V$^{-1}$ s$^{-1}$.[66] In parallel, some copolymers have also been synthesized with modest performances.[67] The low solubility of indolocarbazole-based materials makes the preparation of high-molecular -weight polymers difficult. Tao et al. were the first to obtain the low-bandgap copolymer **P14**.[54] A good solubility was obtained by using 2-hexyldecyl side chains on the nitrogen atoms together with *n*-octyl side chains on the two thiophene units. A $M_n$ of 20 kDa was obtained via a Suzuki coupling reaction. The optical bandgap of this copolymer is 1.89 eV with HOMO and LUMO energy levels at −5.17 and −3.15 eV, respectively. A power conversion efficiency of 3.6% was achieved. The copolymer **P15**, bearing one thiophene on each end of the BT, was synthesized by Hashimoto et al. The bandgap is very similar to the previous copolymer at 1.89 eV. The best PCE obtained with this copolymer was 1.5%.[55] Moreover, the BT monomer bearing two thiophene units on each side was also prepared and the polymerization of this unit with the same IC derivatives presented previously gave **P16**.[56] Lower molecular weights were obtained because of the lower solubility of the monomer. Even with a low $M_n$, the PCE of 2.1% was reported with this material. These performances could certainly be optimized by getting higher molecular weights. It is not an easy task since the addition of longer and bulkier side chains along the conjugated backbone can lead to poor interchain interactions. For instance, Zhang et al. have been able to synthesize the 4,7-dibromo-5,6-bis(octyloxy)benzo-2,1,3-thiadiazole to copolymerize it with 2,7-carbazoles.[68] Their strategy was very effective but the resulting PCE (5.4%) was slightly lower than that obtained with **P10**. However, the authors reported that further optimization of this particular polymer should lead to performances greater than 6%.

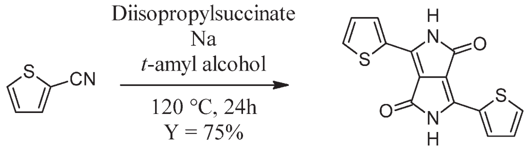

**Figure 6.** Synthesis of the DPP core.

**3.2. Pyrrolo[3,4-*c*]pyrrole-1,4-dione Derivatives.** Even if the BT unit has attracted much attention over the years, there are still other promising electron-deficient comonomers that have been developed for push−pull low-bandgap polymers. One of them is certainly the pyrrolo[3,4-*c*]-pyrrole-1,4-dione also named diketopyrrolopyrrole (DPP) which has a strong absorption in the visible range and usually leads to a good charge-carrier mobility for both holes and electrons. In fact, one of the first organic electronic applications for DPP-based polymers was ambipolar OFETs. Winnewisser et al. were able to synthesize a new polymer having a mobility of 0.1 cm$^2$ V$^{-1}$ s$^{-1}$ for both holes and electrons.[69] Beside these great performances, the DPP core is particularly interesting considering its easy synthesis (see Figure 6).

Accordingly, a large number of low-bandgap polymers have been synthesized since 2008 with the DPP unit and most of them are reported in Figure 7. The homopolymer (**P17**) was synthesized by Janssen et al. through Yamamoto coupling polymerization. They were able to obtain a polymer having a weight-average molecular weight ($M_w$) of 322 kDa.[70] As described by these authors, upon the addition of Ni(COD)$_2$ and bipyridine, the solution became very viscous to the point it had completely solidified. The bandgap of this polymer is very low (1.24 eV). Moreover, the polymer should be stable under ambient condition because of its low-lying HOMO energy level. However, the performances of **P17** in BHJ solar cells were very disappointing with a PCE of only 0.3%. One of the main reasons given by the authors is the energy difference between the LUMO of the donor and the LUMO of the acceptor, which is only 0.18 eV. A difference smaller than 0.2 eV could alter the driving force for the charge separation or can even prevent charge dissociation at the polymer−fullerene interface.[71,72] This phenomenon consistently led to a very low $J_{SC}$ of 0.76 mA/cm$^2$. It is believed that a different electron acceptor could be involved for this particular polymer where the energy difference between the two LUMOs would be higher.

To extend the conjugation of the polymer, we added a third thiophene to the main backbone. The polymerization was performed via a Suzuki cross-coupling polymerization, using 2,5-thiophenebis(boronic ester) as the comonomer.[73] Even with this additional unsubstituted thiophene unit, **P18** shows a very high molecular weight ($M_n$ = 54 kDa). The bandgap of this material remains very low (1.30 eV). The performances are substantially better when compared to those of polymer **P17**. The $J_{SC}$ and PCE values are about 1 order of magnitude higher at

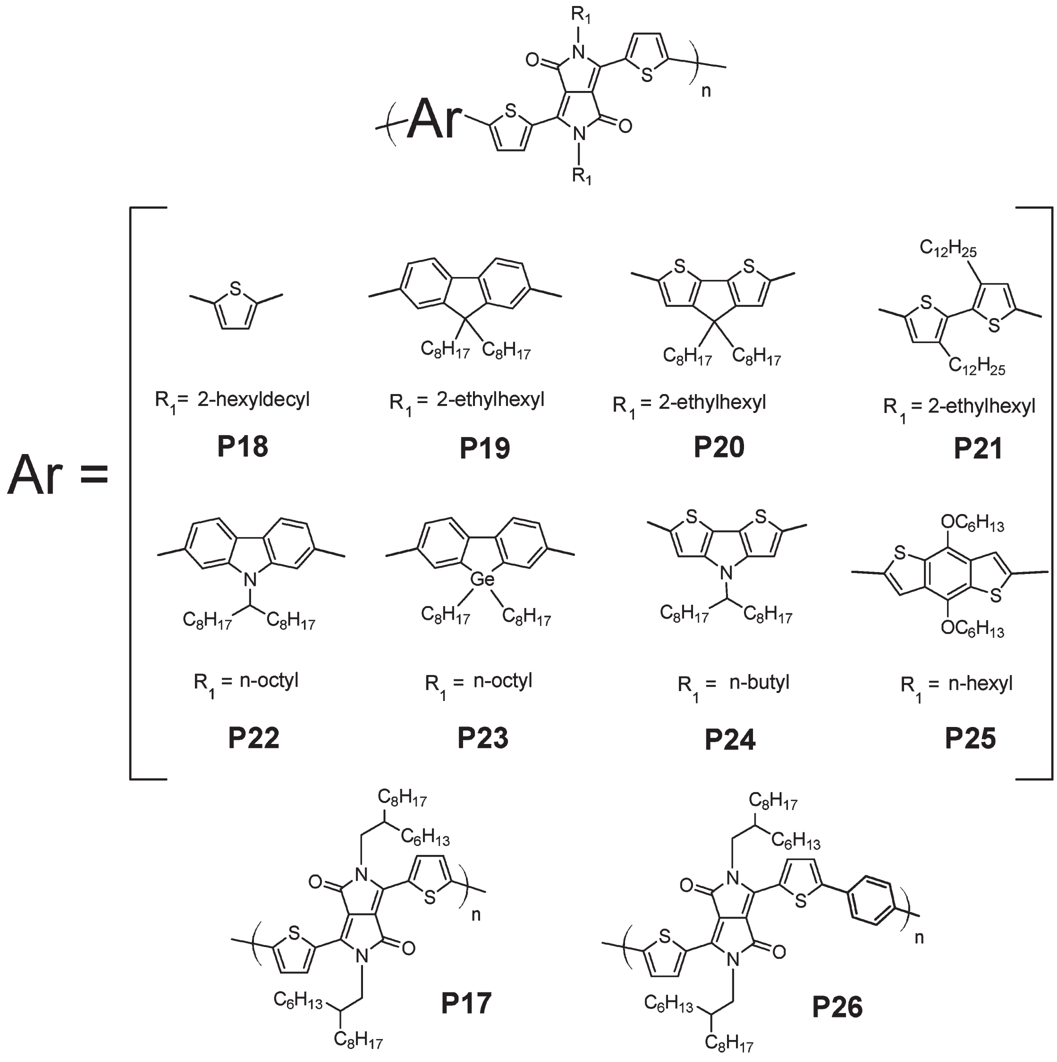

**Figure 7.** Low-bandgap polymers based on DPP used in organic photovoltaic cells.

11.8 mA/cm$^2$ and 4.7%, respectively. The $V_{OC}$ and $FF$ are very similar at 0.64 V and 0.58. In addition to these good performances, field-effect transistors remain very promising with a hole mobility in the $1\times10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ range. This very low bandgap polymer also showed a photoresponse up to 900 nm when combined with PC$_{71}$BM. The DPP core was also polymerized with a bithiophene derivative bearing two *n*-dodecyl side chains to improve the solubility. The $M_n$ of this polymer (**P21**) was 20 kDa and the optical bandgap was 1.40 eV which is about 0.1 eV higher than that of **P17** and **P18**. This is probably due to a torsion angle created by the steric hindrance due to the long alkyl chains on the bithiophene unit. As shown in Table 3, which summarizes all characteristics of the polymers and of the devices, the $V_{OC}$ and FF are very similar to **P17** and **P18**. A power conversion efficiency up to 4.0% has been achieved with this polymer when blended with PC$_{71}$BM and processed with a mixture of solvents (chloroform:ODCB).[74]

As seen for BT derivatives, numerous other electron-rich comonomers have been utilized with the DPP core to try to improve the materials. For instance, Janssen et al. reported copolymers combining DPP and either fluorene (**P19**) or cyclopentadithiophene (**P20**). Suzuki cross-coupling polymerization was employed for these two copolymers and $M_n$ of 17 and 12 kDa have been obtained.[72] The fluorene-based copolymer has a much larger bandgap (1.77 eV) compared to **P20** (1.39 eV). The performances are better with **P20** with a PCE of 1.7% compared to 0.9% with **P19**. This can be partly explained by the very low hole mobility the fluorene-based material which is around 3 orders of magnitude lower than that of **P20** ($1\times10^{-6}$ compared to $1\times10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$). Another reason that the authors gave for these rather low performances is the nonideal morphology of the blended films. Despite many optimizations on this particular point, they could only afford coarser morphology than what is required to achieve great performances. The carbazole derivative was also obtained (**P22**), the bandgap was lower than the fluorene counterpart (1.57 V) and a hole mobility higher than **P21** (0.02 cm$^2$ V$^{-1}$ s$^{-1}$).[75] However, the PCE of the best devices made from this material was only 3.2%. The fill factors were very poor (0.47) and this has adverse consequences on the performances. Leclerc et al. also reported the synthesis and characterization of **P23**, a copolymer based on germafluorene and DPP.[52] Though the performances of **P23** were lower than that of **P12** with a PCE of 1.5%. The authors

**Table 3. Polymer Properties and Device Characteristics for the DPP-Based Polymers**

| polymer | Mn (PDI) (kDa) | $E_g$ (opt) (eV) | HOMO/LUMO (eV/eV) | donor:PCBM ratio (wt:wt) | $J_{sc}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | PCE (%) | active area (mm$^2$) | ref |
|---|---|---|---|---|---|---|---|---|---|---|
| **P17** | 85 (3.8) | 1.24 | −5.29/−3.99 | 1:2 | 0.76 | 0.64 | 0.58 | 0.3 | 16 | 70 |
| **P18** | 54 (3.2) | 1.30 | −5.17/−3.61 | 1:2[a] | 11.8 | 0.65 | 0.60 | 4.7 | 16 | 73 |
| **P19** | 17 (2.2) | 1.77 | −5.43/−3.67 | 1:4 | 2.41 | 0.91 | 0.41 | 0.9 | 16 | 70 |
| **P20** | 12 (1.8) | 1.39 | −5.25/−3.74 | 1:3 | 5.73 | 0.61 | 0.49 | 1.7 | 16 | 70 |
| **P21** | 20 (3.4) | 1.40 | −5.10/−3.40 | 1:2[a] | 11.3 | 0.61 | 0.58 | 4.0 | 9 | 74 |
| **P22** | 30 (2.1) | 1.57 | −5.44/−3.92 | 1:3[a] | 8.6 | 0.80 | 0.47 | 3.2 | 100 | 75 |
| **P23** | 13 (2.8) | 1.63 | −5.38/−3.70 | 1:2[a] | 4.10 | 0.76 | 0.62 | 1.5 | 100 | 52 |
| **P24** | 19 (2.0) | 1.13 | −4.90/−3.63 | 1:4[a] | 14.9 | 0.38 | 0.48 | 2.7 | 6 | 76 |
| **P25** | 19 (1.6) | 1.43 | −5.15/−3.69 | 1:1 | 6.72 | 0.74 | 0.56 | 2.8 | 25 | 77 |
| **P26** | N.A. | 1.53 | −5.35/−3.53 | 1:2[a] | 10.8 | 0.80 | 0.65 | 5.5 | 16 | 78 |

[a] The electron acceptor used is PC$_{71}$BM.

firmly believe that higher molecular weights would lead to higher PCEs.

**P24** is another alternative to get very low bandgap copolymers. This polymer was obtained via a Stille coupling reaction with a good $M_n$ of 19 kDa.[55] As anticipated, the bandgap is very small at 1.13 eV with a HOMO energy level that could bring some stability issues like the other dithienopyrrole (DTP) derivatives (see the previous section). By using *n*-butyl side chains on the DPP derivatives, we obtained a hole mobility of 0.05 cm$^2$ V$^{-1}$ s$^{-1}$. The photovoltaic device made from this polymer reached a very good $J_{SC}$ of 14.9 mA/cm$^2$, which is one of the highest values ever reported for OPVs. Yet, the performances for this polymer are not that impressive because of a $V_{OC}$ of only 0.38 V and a FF of 0.48 which leads to a power conversion efficiency of 2.7% with PC$_{71}$BM in a 1:4 ratio. Finally, benzo[1,2-*b*;3,4-*b*]dithiophene (BDT) is another excellent electron-rich unit which has also been polymerized with the DPP comonomer to give polymer **P25**.[77] Other copolymers based on the BDT unit will be discussed thoroughly in the next section. The polymerization was performed by a Stille coupling reaction where the alkylated tin derivatives were located on both ends of the BDT unit. Because of the ability to add alkyl side chains on both BDT and DPP units, high molecular weights are readily available with these two units. A $M_n$ close to 20 kDa was obtained for **P25** with a bandgap of 1.43 eV. The best PCE for this polymer was 2.8% and to reach this maximum value, the films had to be annealed at 100 °C. When used as cast, the performances were around two times lower, meaning there is a considerable change in the morphology with this thermal treatment. Very recently, Janssen et al. reported an easily accessible copolymer based on the DPP core (**P26**). The only added a phenyl ring to the structure of **P17** by Suzuki cross-coupling polymerization.[78] They could not measure the molecular weight of the polymer because of the formation of aggregates but the other characteristics are very promising. The optical bandgap is of 1.53 eV with HOMO and LUMO energy levels of −5.35 and −3.53 eV, respectively. The best PCE obtained was 5.5% with PC$_{71}$BM in a 1:2 ratio.

It is worth noting that low-molecular-weight diketopyrrolopyrrole derivatives have also been utilized in OPVs.[79] DPP is one of the few units that have allowed good performances without using a polymeric material to carry the holes in the blend. For instance, Nguyen et al. have been able to obtain several low bandgap small molecules (1.5−1.8 eV) with power conversion efficiencies greater than 4%.[80] This value is the highest performance reported for a BHJ solar cell based on a solution-processed conjugated molecular system. This study also shows that with the right combination of functional groups, high molecular weights are not necessary to obtain a strong push−pull configuration, a good morphology, or to achieve high PCEs.

**3.3. Benzo[1,2-*b*;3,4-*b*]dithiophene Derivatives.** Early work on the benzo[1,2-*b*;3,4-*b*]dithiophene unit was directed toward the synthesis of a new alternative to rr-P3HT in field-effect transistor devices.[81,82] Because this unit is completely symmetric, it easily leads to regioregular polymers.[82] Ong et al. were able to obtain a polymer having even more interesting properties than rr-P3HT. It can be noted that the hole mobility is two times higher (0.2 cm$^2$ V$^{-1}$ s$^{-1}$), and in addition, it does not require any thermal treatment after the processing of the films and it is highly stable under ambient conditions.[83] This was a huge step toward air-stable field-effect transistors using solution-processed conjugated polymers as the active layer.

As shown in Figure 8, the synthesis of the BDT core is relatively simple. It is based on a four-step synthesis starting from the thiophene-3-carboxylic acid. The carbonyl chloride is formed by treating the starting component in oxalyl chloride. The diethylamine is then synthesized by taking the carbonyl chloride directly to the next step, without any purification. The final step is a ring closure, which is performed by treating it in *n*-BuLi and subsequently, adding water to the mixture. The overall yield is very good and various side chains can be added at the 4- and 8-positions of the starting BDT.

The promising performances mentioned above contributed to the development of new BDT-based copolymers for photovoltaic cells. The Figure 9 illustrates the wide variety of materials that have been synthesized up to now. The polymer properties and the device characteristics are presented in Table 4. Because the homopolymer has a bandgap higher than 2.2 eV, it is not a viable material for solar cell applications. An electron-deficient functional group or a comonomer that leads to a very planar molecule (thiophene) has to be added in order to reduce the bandgap under 2.0 eV. The first unit used to lower the bandgap of the polymer was a single thiophene unit without any functional group.[84] Polymer **P27** was obtained by Stille coupling polymerization and

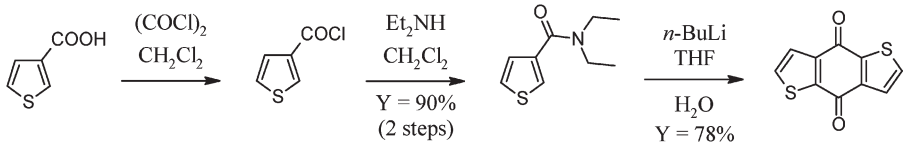

**Figure 8.** Synthesis of the 4,8-dihydrobenzo[1,2-b:4,5-b′]dithiophen-4,8-dione unit.

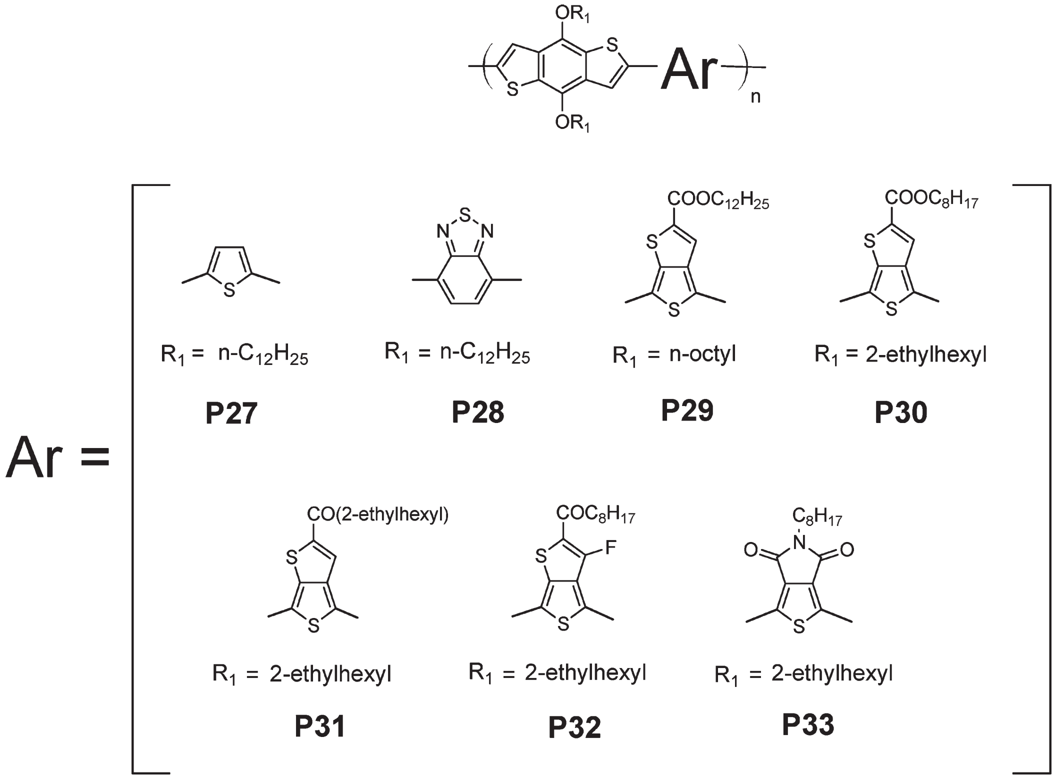

**Figure 9.** Low-bandgap copolymers based on BDT for OPV applications.

**Table 4. Properties and Devices Characteristics for the BDT-Based Low-Bandgap Polymers**

| polymer | Mn (PDI) (kDa) | $E_g$ (opt) (eV) | HOMO/LUMO (eV/eV) | donor:PCBM ratio (wt:wt) | $J_{sc}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | PCE (%) | active area (mm$^2$) | ref |
|---|---|---|---|---|---|---|---|---|---|---|
| **P27** | 47 (1.8) | 2.06 | −5.05/−2.69 | 1:1[a] | 3.78 | 0.75 | 0.56 | 1.6 | 11 | 84 |
| **P28** | 19 (1.7) | 1.70 | −5.10/−3.19 | 1:1[a] | 2.97 | 0.68 | 0.44 | 0.9 | 11 | 84 |
| **P29** | 18 (1.3) | 1.62 | −4.90/−3.20 | 1:1.2[a] | 15.6 | 0.56 | 0.65 | 5.6 | 9.5 | 85 |
| **P30** | 23 (1.4) | 1.62 | −5.01/−3.24 | 1:1[a] | 13.2 | 0.62 | 0.63 | 5.2 | 10 | 87 |
| **P31** | 23 (1.4) | 1.60 | −5.12/−3.35 | 1:1.5[a] | 14.7 | 0.70 | 0.64 | 6.6 | 10 | 87 |
| **P32** | 19 (1.3) | 1.63 | −5.22/−3.45 | 1:1.5[a] | 15.2 | 0.76 | 0.67 | 7.7 | 10 | 87 |
| **P33-a** | 13 (2.6) | 1.80 | −5.56/−3.75 | 1:2[a] | 9.81 | 0.85 | 0.66 | 5.5 | 100 | 90 |
| **P33-b** | 33 (2.3) | 1.82 | −5.43/−3.40 | 1:2[a] | 9.10 | 0.87 | 0.54 | 4.2 | 3 | 91 |
| **P33-c** | 35 (2.7) | 1.73 | −5.40/N.A. | 1:1.5 | 11.5 | 0.85 | 0.70 | 6.8 | 3 | 92 |
| **P33-d** | 16 (6.6) | 1.84 | −5.44/−3.58 | 1:2[a] | 10.3 | 0.91 | 0.51 | 4.8 | 12 | 93 |

[a] The electron acceptor used is $PC_{71}BM$.

the molecular weight was very high (47 kDa). Even though the optical bandgap of this polymer is slightly higher (2.06 eV) than the target for efficient sunlight harvesting, the PCE reached 1.6% with $PC_{71}BM$. Yang et al. were able to lower the bandgap to 1.70 eV with polymer **P28** by using a stronger electron-deficient group (i.e., BT). However, the molecular weight of this polymer is much lower than the previous one and it probably affected the performances of the devices. The best PCE reported with **P28** was only 0.9%. In the same article, the authors also published six other copolymers based on BDT but **P27** was the only material showing a PCE higher than 1%.

Yu et al. developed numerous copolymers based on the BDT that really attracted much interest.[85] They used a thiophene derivative, namely thieno[3,4-*b*]thiophene, as the other comonomer. The thienothiophene derivatives had already been employed before to obtain low bandgap materials.[86] The first thienothiophene developed for photovoltaic purposes contained an ester function with a long alkyl side chain. This functional group should prevent the oxidation of the backbone as well as leading to more soluble materials. **P29** was obtained through Stille polymerization with $M_n$ of 18 kDa and optical bandgap of 1.62 eV. Preliminary performances with this material were very good (PCE of 5.6%).[85] The pristine material showed a hole mobility of approximately $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. The short circuit current density is clearly one of the best in the field at 15.6 mA/cm$^2$. Still, because of the position of the HOMO energy level (−4.90 eV), there are some concerns about the air stability of this polymer. It has to be noted that these results have been obtained without any optimizations or any special treatments of the films.

Further optimizations on the structure and the processing of this class of polymers have been undertaken by Yang et al.[87] First, **P30**, **P31**, and **P32** have been synthesized. **P30** has the same structure as **P29** except for the shorter side chain (*n*-octyl) on the thienothiophene. Surprisingly, this had an effect on the HOMO energy level of the polymer (−5.01 eV) and increased the $V_{OC}$ at 0.62 V. However, the PCE is lower at 5.2% because of the lower $J_{SC}$ and FF. In polymer **P31**, the ester group has been changed to a ketone and the side chain utilized is a 2-ethylhexyl moiety. The $V_{OC}$ for this polymer is higher (i.e. 0.70 V), probably because the HOMO energy level is also lower at −5.12 eV. The resulting PCE with this polymer is very impressive, 6.6% for the best device. Finally, for the last polymer from this study (**P32**), the functional group on the thienothiophene was again a ketone with a *n*-octyl attached to it and a fluorine atom was added at the other free position of the thienothiophene. The fluorine atom had already been used in the literature to increase the $V_{OC}$ of a OPV device because of its high electron affinity.[88] The molecular weight and bandgap of this polymer was very similar with all the other derivatives at ~20 kDa and ~1.6 eV, respectively. As anticipated, the HOMO energy level was again much lower than all the previous materials (−5.22 eV) meaning that the $V_{OC}$ is also better (0.76 V). The best device fabricated with this polymer reached a PCE of 7.7%. The use of different additives such 1,8-diiodooctane allowed a PCE of 7.4%.[89] Recently, Solarmer reported a PCE of 8.1% with this class of polymers.[15]

Following these impressive results, the BDT unit was copolymerized with a thieno[3,4-*c*]pyrrole-4,6-dione (TPD) comonomer. The TPD unit is compact and versatile because of the nitrogen atom which can be functionalized by a wide variety of groups; it also leads to coplanar materials. The synthesis of the TPD monomer is presented in Figure 10, and has been optimized several times.[94]

The first report of a copolymer based on both the BDT and TPD core was made by Leclerc et al. where they added an *n*-octyl side chain on the nitrogen atom of the pyrrole ring. 2-Ethylhexyloxy side chains were also added to the BDT core to increase the solubility of the resulting copolymer. Even with these long bulky side chains, the polymerization, performed by Stille coupling, only led to molecular weight of 13 kDa (**P33-a**).[90] The polymer is readily soluble in chloroform, *o*-dichlorobenzene, and 1,3,5-trichlorobenzene. The HOMO energy level for this polymer is much lower than other BDT derivatives (−5.56 V) which should help to increase considerably the $V_{OC}$ of the devices. The optical bandgap is also interesting at 1.80 eV but is higher than that obtained with the thienothiophene by around 0.2 eV. Devices fabricated with PC$_{71}$BM in a 1:2 ratio allowed the following performances: $J_{SC}$ = 9.81 mA/cm$^2$, a good $V_{OC}$ of 0.85 V, a FF = 0.66; leading to a PCE of 5.5% with an active area of 100 mm$^2$.

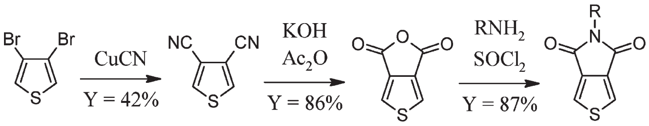

**Figure 10.** Synthesis of the TPD precursors.

Soon after, Jen et al. reported the same polymer (**P33-b**).[91] They were able to increase the $M_n$ up to 33 kDa. Unfortunately, the PCE was more than 1% lower than the first report on this copolymer. Afterward, Fréchet et al. synthesized three copolymers with different side chains on the TPD core. Two new copolymers containing 2-ethylhexyl and 3,7-dimethyloctyl side-chains gave good performances (PCE of 4.0% and 5.7%, respectively), but the best performances were still obtained with the same polymer discussed previously with *n*-octyl side chains (**P33-c**).[92] They reported a PCE up to 6.8% with the addition of 1,8-diiodooctane during the processing of the film. All the device characteristics are very good for this device ($J_{SC}$ = 11.5 mA/cm$^2$, $V_{OC}$ = 0.85 V, FF = 0.70). Finally, Xie, Xhang et al. did also publish an article on the TPD core.[93] The polymers that they reported in their article contain different side chains than those of the previous polymers. On the TPD core, they added a 2-octyldodecyl side chain to enhance the solubility of the resulting material and on the BDT unit, they chose to utilize 2-ethylhexyloxy side chains. This team reported a high $V_{OC}$ of 0.91 V but a relative low fill factor (0.51). By using PC$_{71}$BM and 1,8-diiodooctane during the processing, they reported a PCE of 4.8%. The main conclusion from these four studies is certainly that copolymers based BDT and TPD are very promising. One of the main difference between all the devices characterized to this point is the size of the active area and according to Moliton et al.,[95] this parameter should be considered when comparing different performances.

**3.4. Other Conjugated Polymers.** This last section of the Review will cover other copolymers that did not fit in any previous sections but that are of great importance for the development of the field. Their structures are presented in Figure 11 and the properties of the polymers as well as the device characteristics are summarized in Table 5. One of those so-called exotic polymers was reported by Wong et al.[96] They synthesized a soluble and an intensely colored platinum metallopolyyne (**P34**) with a bandgap of 1.85 eV. Most of these platinum(II) polyynes are usually characterized by relatively large bandgaps, which compare unfavorably with those of some conjugated organic polymers. Successful strategies for creating low-bandgap metallopolyynes involving the construction of push−pull type systems are therefore very scarce.

The solar cells containing a **P34**:fullerene derivative blend as the photoactive material showed a PCE of 4.9% (active layer of 13 mm$^2$ in air) without annealing or utilization of spacer layers. The open-circuit voltage obtained is 0.82 V, the short-circuit current density is 15.4 mA/cm$^2$ with a FF of 0.39. The authors have clearly

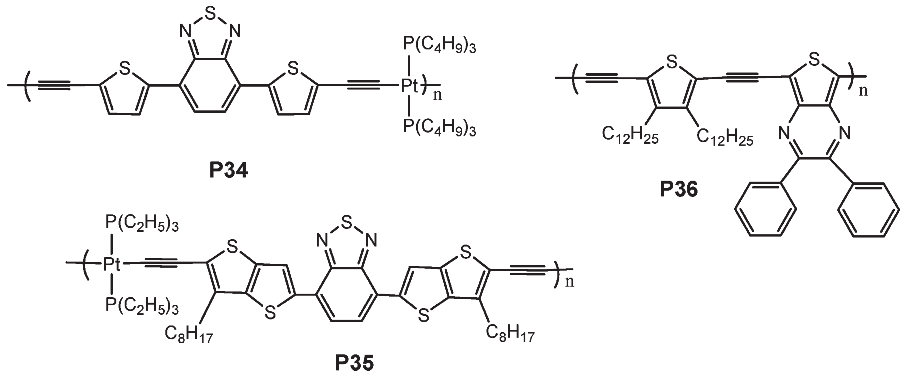

**Figure 11.** Chemical structure of other low-bandgap copolymers.

**Table 5. Polymer Properties and Device Characteristics of the Other Poylmers**

| polymer | Mn (PDI) (kDa) | $E_g$ (opt) (eV) | HOMO/LUMO (eV/eV) | donor:PCBM ratio (wt:wt) | $J_{sc}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | PCE (%) | active area (mm$^2$) | ref |
|---|---|---|---|---|---|---|---|---|---|---|
| **P34** | N.A. | 1.85 | −5.37/−3.14 | 1:4 | 15.4 | 0.82 | 0.39 | 4.9 | 13 | 96 |
| **P35** | 12 (1.7) | 1.81 | −5.14/−3.33 | 1:4 | 9.61 | 0.79 | 0.49 | 3.7 | N.A. | 98 |
| **P36** | 20 (1.5) | 1.57 | −5.22/−3.30 | 1:1 | 10.7 | 0.67 | 0.33 | 2.4 | 25 | 99 |

demonstrated the potential of metalated conjugated polymers in photovoltaic devices. More recently, Jenekhe et al. synthesized a similar organometallic conjugated polymer bearing a platinum center obtained by Sonogashira-type coupling polymerization and evaluated it in BHJ solar cells.[97] The performances of this polymer is significantly lower than those reported by Wong et al., but according to the authors, their results are much closer to the theoretically estimated 2.2% PCE for this polymer.

Jen et al. have designed and synthesized a series of amorphous metalated $\pi$-conjugated polymers exhibiting high field-effect mobilities and high solar-cell power conversion efficiencies.[98] As mentioned above, the most common strategy in designing low-bandgap conjugated polymers is to alternate an electron-rich with an electron-deficient unit along the polymer backbone. However, according to these authors, another approach is to introduce suitable electron-rich organometallic moieties into the polymer main chain. It was reported that polymer **P35**:PC$_{71}$BM blend cast from a chloroform solution gave the best performance as compared to the **P35**:PC$_{61}$BM blend system. Indeed, the results from the electrochemistry and UV−vis absorption studies reveal that the bandgap of polymer **P35** is about 1.8 eV, and the best performance measured for the **P35**:PC$_{71}$BM system leads to a $V_{OC}$ = 0.79 V, a $J_{SC}$ = 9.61 mA/cm$^2$, a FF = 0.49, and a PCE of 3.7%. The improvement in solar cell performances from PC$_{71}$BM compared to PC$_{61}$BM as the acceptor in this polymer can be attributed to the better absorbance and transport properties of PC$_{71}$BM.

Ashraf et al. also reported the synthesis of the low bandgap polymer **P36**, (poly[3,4-didodecylthiophene-2,5-diylethynylene-(2,3-diphenylthieno[3,4b]pyrazine-5,7-diyl)ethynylene]).[99] Thieno[3,4b]pyrazines have been shown to be excellent precursors for the production of low bandgap conjugated polymers. This polymer utilizes a push−pull approach to achieve absorption in the visible region (390−800 nm). The bandgap is 1.67 eV. The cell based on **P36**:PC$_{61}$BM blend has a $V_{OC}$ = 0.67 V, a $J_{SC}$ = 10.72 mA/cm$^2$, a FF = 0.33, and a PCE = 2.4%.

## 4. Summary and outlook

As clearly shown above, the field of organic photovoltaic cells is literally exploding with power conversion efficiencies now reaching 8%. However, there is still a need for new low-bandgap polymers as well as new developments in the fabrication of the OPVs to obtain higher efficiencies. From a materials viewpoint, the requirements are still a HOMO energy level lower than −5.20 eV, a bandgap in the 1.30−1.90 eV range, and a hole mobility greater than $1 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$.[14] As shown in Figure 12, all the polymers that have power conversion efficiencies higher than 5% show a bandgap in the ideal range.

Figure 13 teaches us that even if the bandgap is in the desired range, it does not ensure good performances because there are other parameters that interfere like the HOMO energy level of the material which directly influences the $V_{OC}$ and the air stability of the devices. The morphology of the bulk heterojunction is an important parameter. As seen in this review, there are a lot of promising materials that have been developed and many of them showed poor PCEs. This highlights the importance of optimizing the films and the devices because each polymer responds differently to the processing conditions.

In parallel, the fabrication of tandem solar cell is another interesting way to fabricate polymeric solar cells which could allow better performances.[100] Janssen et al. have achieved performances close to 5% with a dibenzodithiazole and a diketopyrrolopyrrole derivative.[101] The best performances obtained with this new technology has been reported by Heeger et al. with a PCE of 6.7%.[102] The best theoretical performance for this type of device is about 15%.[103] Recently, Janssen et al. described an all solution-processed device fabrication, which is a great step forward for the fabrication of these cells.[104]

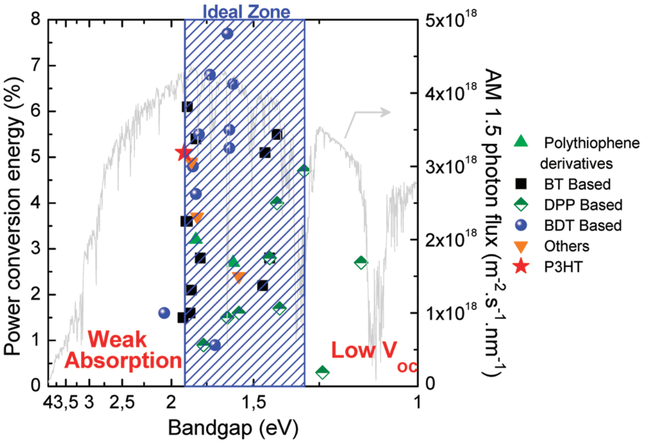

**Figure 12.** PCE compared to the bandgap for all the presented polymers in this review.

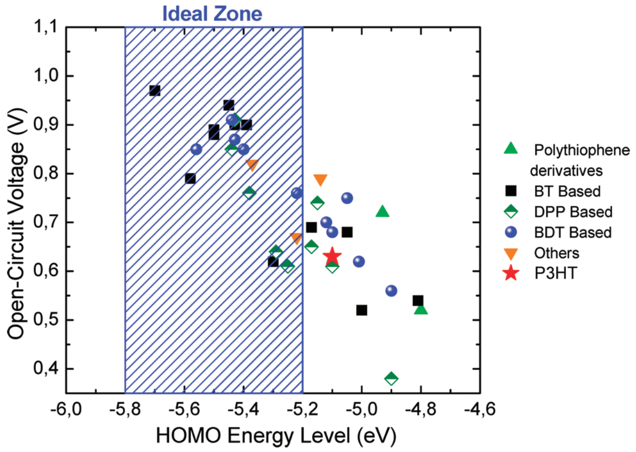

**Figure 13.** $V_{OC}$ in BHJ solar cells as a function of the HOMO energy level of the polymeric donor.

The synthesis of new soluble and stable *n*-type polymers that could replace the fullerene derivatives is also underway.[105] These polymers should have a broad absorption spectra that would be complementary to the absorption spectra of the *p*-type material and a high electron affinity with a low-lying LUMO energy level to facilitate the electron transfer. Unfortunately, the performances obtained with this type of materials are not yet close to that ones obtained with $PC_{61}BM$ and $PC_{71}BM$.

Finally, it is clear that to achieve power conversion efficiencies around 10%, an interdisciplinary approach is required. From the synthesis of new materials to the engineering of the devices, every aspect of the fabrication of a solar cell has to be optimized. This review was an attempt to describe the new exciting polymers that have been made over the past few years and hopefully, it will stimulate scientists to go beyond the 7−8% efficiency of current materials. Interestingly, during the preparation of this review, Tao et al. have reported the first *s*-tetrazine-based low-bandgap polymer, with a power conversion efficiency of 5.4%, which indicates a permanent and growing creativity in the synthesis of processable low bandgap conjugated polymers for photovoltaic applications.[106]

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